

Ottawa, Canada  
K1A 0C9

(21) (A1)	2,066,149
(22)	1992/04/15
(43)	1992/11/23

5,028,0/66

(51) INTL.CL.<sup>5</sup> B05D-001/08; C23C-026/02

(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Method for Coating a Fibre-Reinforced Plastics Body

(72) Habenicht, Hinrich - Germany (Federal Republic of) ;

(73) Sigri G.m.b.H. - Germany (Federal Republic of) ;

(30) (DE) P 41 16 641.8 1991/05/22

(57) 18 Claims

Notice: The specification contained herein as filed

**Canada**

CCA 3254 (10-89) 41

## Abstract

### Method for coating a fibre-reinforced plastics body

5        For the application of a firmly adhering  
resistant, metal or ceramics coating to bodies  
consisting of reinforcing fibres and a synthetic resin  
matrix by means of a thermal spraying process, there is  
introduced into the surface of the fibre-reinforced  
10 synthetic resin body facing the subsequently applied  
thermally sprayed layer, a material in particle form  
which is capable of combining chemically with the  
material serving as a thermal coating material. Before  
thermal spraying takes place, the surface of the body  
15 to be coated is removed in such a way that clean  
exposed surfaces of the dispersed particles result,  
enabling the bonding of the layers.

The invention relates to a method for the application of at least one firmly-adhering resistant coating layer to a surface of a body made of a composite material of reinforcing fibres and a plastic matrix.

By the use of fibre-reinforced plastics, considerable advantages can be achieved in mechanical engineering, vehicle and plant construction as well as in the building industry. Fibre-reinforced plastics are generally lighter than metals, have good corrosion resistance and, with an appropriate design, at least equally good mechanical properties in relation to weight. These advantages are particularly evident in the case of rapidly moving parts such as, for example, shafts, cylinders, rollers, tappets, levers or propellers, etc.

Rapidly rotating rollers made of metals, for example for paper and foil manufacturing and processing or printing machines are, because of their heavy weight, subject to considerable centrifugal forces, the inertial forces as well as motive forces are relatively great, and large demands are made on the weight balance. Nowadays, therefore, rollers used for this purpose are made of fibre-reinforced plastics, in particular carbon fibre-reinforced plastics, which have a substantially smaller weight than rollers made of metal, with the same rigidity and improved dimensional stability (DE-GM 83 22 639).

In plant construction and in tank construction, as well as in the building industry, it is advantageous to make use of the high level of tensile and bending strength, the outstanding torsional rigidity and the corrosion resistance of the reinforced

plastics materials, which are lighter in comparison with metals or ceramics materials.

When the surfaces of fibre-reinforced plastics are used for conveying or transporting operations, or when they are acted upon by substances which are in motion relative to these surfaces, however, they frequently prove to be too poorly resistant thereof. For reducing abrasion phenomena and preventing product contamination, it has therefore been proposed to coat the surfaces with a resistant metal by electrolytic deposition, (DE-GM 84 06 019).

10 The quality of layers applied in this way, however, is unsatisfactory in many cases because of insufficient adhesion. According to another process (GB 887 366), moulded bodies made of hardenable plastics, such as formaldehyde resins, are provided by flame spraying with coatings made of metals or alloys which are intended to make these parts resistant to collision and impact stresses. This process is complicated and expensive according to the present state of the art. In addition, the adhesion of the layers is unsatisfactory for modern requirements, in particular when under dynamic stress, and the choice of materials which can  
20 be sprayed on and can be combined is limited. In order to obtain layers with sufficient adhesion, special requirements must in fact be observed. The material for the first layer cannot be freely selected. Its melting point must be 400°C above the decomposition point of the plastics and its thermal expansion coefficient must be greater than that of the plastics. Furthermore, it is required that the material from which the second layer is to be built up has a smaller expansion coefficient than the previously applied first layer, and this already indicates

poor adhesion of the first layer to its substrate. The plastics parts to be coated can contain fillers such as coke powder, graphite, wood dust, rock flour, quartz powder, paper or textile shreds, which are possibly to serve for lowering the thermal expansion coefficient. Participation of this filler in the anchoring of the metals sprayed on to the plastics surface is not indicated in the text, and is not possible because of the differences between the filler and the coating material.

Swiss Patent No. 538 549 also deals with the application by flame spraying of protective layers to plastics parts produced from synthetic resin, fillers and/or fibres. According to this patent, protective layers can be applied according to the flame spraying process, but these layers have unsatisfactory adhesion, or irreparable damage occurs to the surface of the support substance. In particular, damage to the reinforcing fibres is caused by the method. In order to solve the problems, therefore, there is first applied to the fibre-reinforced basic body an intermediate layer made from a fabric or net and a synthetic resin, which layer serves as an adhesion primer and buffer during flame spraying. The sprayed-on particles penetrate between the individual fabric pores and thus achieve deep anchoring. This method is not technically satisfactory either and is also expensive, because the manufacture of the intermediate layer is only possible with substances which are available in fabric or net form; the processing of fabrics and braids requires expensive hand working or special technical apparatus and the fabric or braid must be matched precisely to the surface of the

base body, which causes problems, in particular in the case of closed surfaces, because of the occurrence of butt joints or overlapping. This fabric-containing layer serves as a thermal barrier during flame spraying. It is therefore subject to high internal stresses caused by differences in the thermal expansion coefficients between the synthetic resin matrix and the material of the fabric. These stresses can, with an outer sprayed-on layer which adheres quite well, lead to internal defects and delamination in the base body. However, the bonding of the sprayed-on layer also leaves something to be desired, in spite of improvements over the prior art since, during flame spraying, in all cases the hot particles first meet a synthetic resin surface which then decomposes to a greater or lesser extent and, as tests have since shown, prevents the direct chemical bonding of the sprayed material to appropriately chosen fabric or net material.

In German Patent No. DE 35 27 912, another method for coating carbon fibre-reinforced plastics bodies with metals is described. Good bonding of the protective layer is achieved with this method by using the plasma spraying method in combination with a carbon fibre-reinforced substrate surface which is based on a phenol formaldehyde resin. This method has indeed entered into industrial practice, but the durability of layers produced according to this method is not completely satisfactory, either. In the case of large mechanical loads such as those occurring during cutting up, grinding to size, under an impacting load or even a long operating load, delamination of the coating still occurs.

Thus, in the invention it is attempted to provide an improved method of the type described above, in which method the choice of synthetic resin used as a matrix and the choice of the substance used for the coating are not subject to restrictions, the manufacture of the composite body which is capable of coating and of the coated composite body is simple and low-cost, and layers having substantially improved adhesion can be produced.

10 According to the invention, the surface to be coated has an outer layer made of a synthetic resin in which particles are incorporated. The particles are made of a material corresponding, as material, to the material which serves as the resistant coating layer or which is capable of bonding chemically with the material serving as the resistant coating layer. A surface of the outer layer is removed to such an extent and in such a way that the particles which are integrated into the surface have clean exposed surfaces free from the synthetic resin and pointing in the direction of the later coating. The material for producing the resistant coating is sprayed on the thus-treated surface by means of a thermal spraying operation.

20 The following, interacting factors are essential to the invention:

1. A base body made of fibre-reinforced plastics is bonded to a layer of a synthetic resin containing particles. The synthetic resin used for this layer shows, on the one hand, good bonding to or into the resin matrix of the base body and, on the other hand, good ability to retain the particles which may be granular to powdery.

2. The surface of the particle-containing outer layer is removed, in the cured state, to the extent that the particles, first coated with a layer of synthetic resin when subject to manufacturing conditions, have clean, exposed, outwardly directed surfaces, but, on the other hand, remain firmly anchored to the synthetic resin matrix.

10 3. The first layer applied to this surface by means of a thermal spraying process anchors itself to and into the exposed surface portions of the particles which, on their unexposed sides, are firmly retained in the synthetic resin matrix of the intermediate layer. This anchoring is produced by a chemical bonding of the sprayed-on particles to the substrate particles embedded in the resin matrix. The lack of a synthetic resin skin covering the particle surfaces is essential for the satisfactory formation of such a bond. Tests have shown that the bonding of the thermally sprayed-on layer is drastically worsened if the hot particles must first break through a synthetic resin skin before they reach the surfaces of the particles anchored in the synthetic resin layer, or if they hardly achieve only a  
20 mechanical hold in the synthetic resin layer. Products of thermal decomposition which are produced upon the impact of the hot, molten coating particles with a synthetic resin surface, are also an obstacle to bonding. In contrast to all previously known methods, anchoring of the thermally sprayed-on layer in the synthetic resin substrate is no longer necessary with the method according to the invention.

The base body made of fibre-reinforced plastics may have any shape suitable for the use of a thermal spraying method.

A group of preferred bodies are flat or curved areal moulded bodies such as plates, bowls, containers or pipelines or segments thereof. Another group of preferable bodies have at least partially closed surfaces such as pipes, rollers, cylinders, cones or truncated cones.

10 Any synthetic resins from which bodies of the shape described above can be manufactured with sufficient stability of shape and temperature can be used as the base material and matrix material for the reinforcing fibres. In particular, preferred are thermosetting resins such as phenol formaldehyde, epoxy or polyester resins. However, thermoplastic resins such as, for example, polypropylene, polyamide or polycarbonate are also suitable. Carbon fibres (with graphite fibres being included in this term), glass fibres and arylamide fibres are particularly preferred as the reinforcing fibres. Where useful, other fibres, for example mineral fibres such as basalt fibres or rock wool, metal fibres and carbide fibres such as SiC whiskers, can also be used. The fibres can be incorporated into the synthetic resin body as short-chopped fibres or staple fibres, in the form of  
20 woven cloth, nets, knitted fabrics or other textile formations of two-dimensional or three-dimensional kind, or as continuous filaments.

Serving to provide bonding for the layer to be sprayed on thermally are particles which are incorporated either:

1) directly into a layer adjacent to the outer surface of the fibre-reinforced base body or

2) in a layer applied to the outer surface of the fibre-reinforced base body and firmly bonded to this surface.

In the first case, the particles are worked in directly during the formation of the outermost layers. The particles in the dry state can be processed. The particles may also be provided with a bonding agent or suspended in a resin or in a resin solution. This can take place, for example, by the simultaneous spraying-on of the particles and a short-fibre-reinforced synthetic resin material, using separate spraying devices operating in coordinated manner, or by the spraying-on of the synthetic resin containing the particles in a suitable manner, or by sprinkling the dry particles during the formation of a body reinforced with filaments, for example during the winding process.

In the second case, there is produced in an advantageous manner a mixture made of a synthetic resin which can bond well to the base body made of fibre-reinforced synthetic resin, and the particles. The synthetic resin selected for this purpose may be the same as that of the base body or it may be another which is capable of bonding well to the base body, of retaining well the particles and of being well machined after curing. This mixture of the synthetic resin and the particles is applied in a thin layer to the surface of the fibre-reinforced synthetic resin body. Any methods which are suitable for this can be used. The application can be carried out for example by hand with a spatula, mechanically with a doctor blade, by a spraying operation or, according to an "inverse method". The "inverse method" involves inflating a body, especially a cylinder or a tube, against a correspondingly shaped mould, the inner wall of which has been provided with a synthetic resin and particle

layer, curing of the synthetic resin and subsequent removal from the mould. According to another variant of such an "inverse method", a synthetic resin is used which expands during temperature treatment and/or during curing. The particles may possibly be contained in the expandable synthetic resin or in a synthetic resin layer applied to the inner wall of the surrounding mould. For coatings which do not need to satisfy any high demands, the particles can also be sprinkled on to a synthetic resin layer or sprayed on as powder and, if necessary, pressed in. After its  
10 production, the particle-containing layer is cured according to known methods.

When high demands are made of the dimensional accuracy of the finished coated body, it is advantageous to provide the fibre-reinforced base body with a surface which is machined to suitable tolerances. This can be carried out, according to use, by a grinding or machining operation. In order to obtain a smooth undeformed surface after the application of the particle-containing synthetic resin layer and the curing of this layer, the body provided with the particle-containing synthetic resin  
20 layer may be coated with a covering foil which is removed after curing. For this purpose, a cylindrical body may be wound with a covering band in a manner known in the art. The thickness of the layer located on the fibre-containing base body and containing particles acting as agent for the bonding of the thermally sprayed-on layer is not particularly critical and is generally from 50  $\mu\text{m}$  to 4,000  $\mu\text{m}$ . The layer thinner than 50  $\mu\text{m}$  is unlikely to permit sufficient thermal compensation during thermal spraying

and tends to result in a break bonding. On the other hand, the layer thicker than 4,000  $\mu\text{m}$  may not be very favourable because of increased consumption of material, increased weight of the whole body and because of difficulty of applying the coating in a dimensionally accurate manner. The particles which act as a bonding agent may be introduced into the synthetic resin in granular or powder form. The amount of the particles may vary in a wide range according to requirements in each case, is preferably between 5 and 60 percent by volume, relative to the mixture of the synthetic resin and the particles. The shape of the particles can vary in each case according to the origin of the material and the method of its production. The most frequently used forms are essentially isometric, platelet or rod shape while those having angular, rough or serrated particle surfaces tend to form firm anchoring and thus are preferred. The particle size is not particularly critical and is generally from 10  $\mu\text{m}$  to 1,000  $\mu\text{m}$ .

The particles introduced into the body to be coated correspond to the materials of which the thermally sprayed-on layers are formed. These can be metals such as nickel, chromium, vanadium, manganese, iron, cobalt, titanium, silicon, alloys of these metals or aluminium or alloys thereof or copper and alloys thereof or non-metallic substances such as silicon dioxide, glass, aluminium oxide, titanium dioxide, zirconium dioxide or Si-SiC. With the coating as a whole in mind, proceeding from the requirements for the thermally sprayed-on layer, a material is chosen which results in good bonding to the material of the thermally sprayed-on layer and which can be firmly anchored in

particle form in the resin matrix. At the same time, it is not necessary that the particles anchored in the synthetic resin consist of the same material as the thermally sprayed-on layer.

After curing the layer containing the particles, the synthetic resin skin initially covering the particles is removed. This is absolutely necessary for the further success of the method according to the invention for good chemical bonding to be achieved between the thermally sprayed-on layer and the particles acting as agent for the bonding of this layer to the fibre-reinforced body. The removal may be accomplished, for example, by a mechanical removal, by a chemical dissolution or an etching process. Particularly advantageous as the mechanical removal are machine grinding and sand or powder blasting. The relatively smooth particle surfaces obtained in this way can subsequently be roughened, for example by a chemical etching with an acid or an alkali, without damaging the smooth synthetic resin surface of the body. The term "chemical bonding" in the present invention includes any types of chemical bonding such as ionogenic, covalent, metallic and dative bonding.

When dimensionally accurate coated parts such as rollers for the printing industry are to be manufactured, it is advantageous to grind to size the surface of the cylinder blank after application of the particle-containing layer but before the thermal coating, to form a smooth surface. The layers which are subsequently sprayed on thermally and possibly layers which are applied additionally then have a more uniform layer structure and a more uniform layer thickness and can be brought to the

required size and required surface quality at a lower cost.

At least one layer is sprayed on to the fibre-reinforced synthetic resin body premachined as described above, which body has a particle-containing zone on the outside, by means of a known thermal spraying method. Flame spraying and plasma spraying, in particular, including variants of vacuum plasma spraying, are possible as the method of application. The resistant coating layer is typically formed of a resistant metal such as nickel or an alloy mainly composed of nickel. The resistant coating layer may also be formed of a ceramic material such as aluminium oxide.

Any of the substances listed above as dispersion material in particle form for the synthetic resin intermediate layer can be used as spraying material. The selection of the substance used in each case depends on the specific application. The application also determines the structure of the surface of the body. The coated body can frequently be used without further surface treatment for uses in the building industry or in abrasion protection. Uses in mechanical engineering such as, for example, printing, inking, idle or feed rollers in paper or foil production or processing require subsequent processing by metal removal machining operations, by grinding, polishing or lapping, in order to achieve the necessary degree of precision and surface roughness.

Many uses require the production of bodies with a multi-layer coating on the base body containing synthetic resin. This can be the case, for example, when, on the outside, a ductile surface is required which is supported on a hard tough substrate

or, in general terms, when the application of a primary layer alone is not sufficient for the intended use, and the required properties of the coating with regard to hardness, roughness, adhesion, porosity, electrical conductivity, surface structure etc., can only be achieved by applying further layers. In these cases it is possible to apply further layers to the first thermally sprayed-on layer, according to methods known per se and tested in practice. This can be carried out by continuing the application with thermal spraying methods or, if the primary layer is electrically conductive, even electrolytically. In this way, several layers can be applied one on top of another. The application method used may vary from layer to layer. The materials which are applied in layers one on top of another are usually formed from different substances. However, they can also be of identical material.

As can be seen, the method according to the invention can be varied a great deal and permits, in a simple way, adaptation to a large number of approaches to technical problems. In detail, the following advantages result. It is now possible to produce, in a simple way, on fibre-reinforced synthetic resin bodies, by means of a thermal spraying method, surface coatings with considerably improved adhesion and mechanical stability in comparison to the prior art. The earlier problems of bonding existing between the thermally sprayed-on layer and the fibre-reinforced synthetic resin body, which were caused by:

- 1) the effect of great differences in thermal expansion coefficients between the fibre-reinforced synthetic resin body

and the thermally sprayed-on coating material and

2) the formation of decomposition products of the synthetic resin during the thermal spraying and

3) the production of such decomposition products during thermal spraying and/or the presence of a synthetic resin intermediate layer between layers applied additionally to the fibre-reinforced synthetic resin body in order to produce better bonding of the sprayed-on layers, and the thermally sprayed-on layer,

10 have become practically insignificant for the thermal spraying-on of the layers and for the stressing of these layers in the course of operation. The lack of sensitivity and the good adhesion of the coating can be seen in the fact that bodies coated using the method according to the invention can be cut with mechanical cutting tools without parts of the layer being chipped off, and that the coating stands up to impact stresses during handling and in operation, without damage. The application and preparation on the fibre-reinforced base body, of the layer required by the procedure and determining the improved adhesion, can take place  
20 according to methods which are simple and can also be carried out mechanically, and thus efficiently. Damage to outer reinforcing fibres by the impact of particles during thermal spraying can be excluded. The user of the method is free, within wide limits, in his choice of resin matrices for the reinforcing fibres and the materials for the layers to be applied.

The invention is explained by the following exemplifying embodiments. However, it is not limited to the embodiments in the examples.

Example 1

A 2,000 mm long hollow cylinder having an internal diameter of 90 mm and made of phenol formaldehyde resin reinforced with carbon filaments was used as a starting material. The cylinder was produced by winding a carbon fibre saturated with phenol formaldehyde resin on to a cylindrical mandrel in a large number of layers, curing the resin, and removed from the mandrel. The cylinder was ground to size on a turning lathe so that it had an outside diameter of 100 mm. For coating with a synthetic resin layer filled with a metal powder, the cylinder prepared in this way was clamped on to a digitally controlled winding machine and its outer surface was degreased with acetone. The composition for the coating consisted of a mixture of phenol formaldehyde resin (Bakelite\* DW 247), with a viscosity of 500 to 1,000 mPa·s and water-atomized steel powder (type 316 L) which is rust-free and has a granular size  $\leq 75 \mu\text{m}$  in the volume ratio 45% steel powder to 55% phenol formaldehyde resin. For the coating, the cylinder was rotated at a speed of 30 m/min and the coating mixture was applied with a flexible spatula to a thickness of approximately 1 mm. Subsequently, the coated body was wrapped around with a tear-off fabric and cured in a circulating air drying cabinet with the following hardening cycle:

Heating to 90°C, 1 hour,  
Holding time at 90°C, 24 hours,  
Heating from 90°C to 130°C, 1 hour,  
Holding time at 130°C, 2 hours,

\* Trade-mark

Cooling to room temperature without active cooling.

The cylinder having the cured surface layer was ground to size to a diameter of 100.8 mm and a surface roughness of 10 to 15  $\mu\text{m}$ , on a grinding machine with a diamond wheel and its outer surface was dusted off by blowing with oil mist-free compressed air. A layer made of a nickel/chromium alloy (80% by weight nickel, 20% by weight chromium) was applied to the lateral surface of the cylinder prepared in this way by plasma spraying and applying the conventional conditions for this technical field. After the spray treatment, the peaks and edges of the applied coating were removed by brushing with a wire brush and a smooth surface was obtained.

#### Example 2

A large carbon fibre cable made up of 40,000 filaments which had been led through a bath of an epoxy resin (Bakelite\* L 20) with viscosity 800 to 1,000 mPa·s, was wound on a winding machine, on to a mandrel 90 mm in diameter to a layer thickness of approximately 9.5 mm. The wound body had a length of 1,500 mm. For introducing the metal-containing layer of bonding agent into the outer layers of the wound body, work was continued with a carbon fibre cable made up of 12,000 filaments. This cable was led through a bath which consisted of a suspension made of the same epoxy resin as above (Bakelite\* L 20) with a content of 50% by weight (= 15% by volume) of an alloy powder having a granular size  $60\% \leq 70 \mu\text{m}$  and a composition of 89% by weight nickel, 5% by weight molybdenum and 6% by weight aluminium, and, after passing through the bath until a wall thickness of approximately 10.1 mm had been achieved, the cable was wound on to the cylinder.

Because of the fibre tension during winding, a considerable part of the mixture of epoxy resin and alloy powder was pressed out of the wound layers applied in this way, into the outer surface layer, so that a thin, fibre-free layer of synthetic resin and alloy powder was formed there. The surface of the wound body was wrapped around with a separating foil and cured in a circulating air drying cabinet with the following hardening cycle:

Heating to 90°C, 1 hour,  
Holding time at 90°C, 10 hours,  
Heating from 90°C to 130°C, 1 hour,  
Holding time at 130°C, 2 hours.

The cylinder obtained in this way was then ground on a turning lathe with a diamond grinding wheel to a final size of 10.0 mm. For coating the cylinder after the flame spraying operation, the cylinder was clamped after grinding, into a motor-driven turning device which enabled rotation of the cylinder around the longitudinal axis. Before the start of the spraying operation, the surface of the cylinder was cleansed of particles of dust adhering to it by means of oil mist-free compressed air. Subsequently, the lateral surface of the cylinder was coated with a 100 µm thick layer made of an alloy composed of 78% by weight nickel, 15% by weight chromium, 7% by weight iron by the flame spraying procedure under conventional conditions for this branch of technology. After coating, the surface of the cylinder was smoothed by removing the peaks by means of a steel brush.

### Example 3

A mixture of phenol formaldehyde resin (Bakelite\* DW 247, viscosity 500 to 1,000 mPa's) with an alloy powder (grain sizes 100 to 200  $\mu\text{m}$ , composition: nickel 80% by weight, chromium 20% by weight) in the volume ratio 55% alloy powder, 45% phenol formaldehyde resin was applied with a spatula, to a plate (width 30 cm, length 50 cm, thickness 0.2 cm) reinforced with glass fibres (average length 20 mm) and made of phenol formaldehyde resin, the surface of which had been freed of dust with oil mist-free compressed air, to a layer thickness of 1 mm. For hardening the layer applied, the plate was placed in a circulating air drying cabinet and cured according to the hardening cycle described in Example 1. After curing, the surface of the plate was treated with a sand blaster until approximately 0.1 mm of the cured resin layer applied to the surface of the plate and containing alloy powder had been removed and sufficient surface portions of the grains of alloy powder dispersed in the resin layer had been blasted free of resin. After blowing free of dust with oil mist-free compressed air, the blasted surface was provided with an aluminium oxide layer (layer thickness 500  $\mu\text{m}$ ) in a plasma spraying installation having a two-coordinate traversing device (horizontal, vertical). The coating thus obtained can be used without further machining for the purpose of abrasion protection.

The thermally sprayed-on layers produced in with the coatings according to Examples 1, 2 and 3 were compared with layers of identical composition which had been manufactured

without the use of an intermediate layer enabling bonding, using coating methods according to the prior art. The test methods and types of stress applied, and the test results obtained and observations made, can be seen from the tabulated summary.

Type of stress/ test method	Example 1	Comparison	Example 2	Comparison	Example 3	Comparison
Tear-off test with stuck-on stamp.	Tearing of the adhesive from the surface of the coating.	Tearing of the coating from the cylinder surface.	Tearing of the adhesive from the surface of the coating.	Simple parting of the coating from the cylinder surface during tearing off.	Tearing off within the adhesive layer.	Sprayed-on layer shows cracks after application and partially chips off during mechanical stressing.
Cutting or parting of the body to size by means of diamond-studded parting wheel or band saw.	Clean cut, no continuing cracks or chipping off.	Clean cut, with, in 30% of the bodies, cracks extending at an angle from the parting plane and with chipping off in 10% of the bodies.	Clean cut, no continuing cracks or chipping off.	Cut, with slight (up to 0.05 mm deep) eruptions in the layer. Increased crack formation on the parting edge (45% of the bodies), chipping off in 30% of the bodies.	Clean cut, no continuing cracks or chipping off.	- " -

To these observations and results it must be added that coating operations such as those carried out in Examples 1, 2 and 3, but without first freeing and cleansing from synthetic resin the bonding surfaces of  
5 the particles incorporated in the synthetic resin intermediate layer, only achieve adhesion of the quality in the comparison example to Example 1.

The results described show clearly the technical progress brought about by the invention.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A method for the application of a firmly adhering resistant coating layer to a body made of a composite material comprising reinforcing fibres and a plastic matrix, which process comprises:

(A) providing the body having an outer layer made of a synthetic resin containing particles of a material incorporated therein which corresponds to or is capable of chemically bonding with a material of the resistant coating layer;

(B) removing a surface of the outer layer to such an extent and in such a way that the particles have a clean exposed surface free from the synthetic resin and pointing in the direction of the later resistant coating; and

(C) spraying the material of the resistant coating layer onto the surface by means of a thermal spraying process.

2. The method according to claim 1, wherein the outer layer of the synthetic resin containing the particles has a thickness of from 50  $\mu\text{m}$  to 4,000  $\mu\text{m}$ , and the particles are incorporated in an amount of 5 to 60% by volume relative to the total amount of the particles and the synthetic resin.

3. The method according to claim 1, wherein the particles have a size of from 10  $\mu\text{m}$  to 1,000  $\mu\text{m}$ .

4. The method according to claim 1, 2 or 3, wherein the particles and the material used for the thermal spraying are each made of a metal selected from the group consisting of (a)

nickel, chromium, vanadium, manganese, iron, cobalt, titanium, silicon, or alloys of these metals, (b) aluminium or aluminium alloys, and (c) copper or copper alloys.

5. The method according to claim 1, 2 or 3, wherein the particles and the material used for the thermal spraying are each made of a non-metallic substance selected from the group consisting of silicon dioxide, aluminium oxide, titanium oxide, zirconium oxide and silicon carbide/silicon.
6. The method according to claim 1, 2 or 3, wherein the composite material is reinforced with short fibres.
7. The method according to claim 1, 2 or 3, wherein the composite material is reinforced with filaments.
8. The method according to claim 1, 2 or 3, wherein the composite material is reinforced with textile structures obtained by textile linkage of fibres.
9. The method according to claim 1, 2 or 3, wherein the outer firmly adhering, resistant layer is applied by flame spraying.
10. The method according to claim 1, 2 or 3, wherein the outer firmly adhering, resistant adhesive layer is applied by plasma spraying.
11. The method according to claim 1, 2 or 3, which further comprises thermally spraying at least one further layer onto the thermally sprayed-on layer.

12. The method according to claim 1, 2 or 3, which further comprises electrolytically depositing at least one layer on the thermally sprayed-on layer.

13. The method according to claim 1, 2 or 3, wherein the body to be coated is a cylinder or roller made of carbon fibre-reinforced synthetic resin.

14. A method for the application of a firmly adhering abrasion-resistant coating layer of a metal or ceramic material to a body made of a composite material comprising reinforcing fibres and a plastic matrix, which process comprises:

[A] on a surface of the body, forming an outer layer which is firmly bonded to the body, has a thickness of 50  $\mu\text{m}$  to 4,000  $\mu\text{m}$  and is made of a cured synthetic resin containing particles of a material incorporated therein, the said material of the particles being a metal or ceramic and being capable of chemically bonding to the material of the abrasion-resistant coating layer, wherein the outer layer is formed as an outermost part of the body during the production of the body or is formed as an additional layer after the production of the body;

[B] removing a surface of the outer layer to such an extent and in such a way that the particles have a clean exposed surface free from the synthetic resin and pointing in the direction of the later abrasion-resistant coating and are firmly anchored to the cured synthetic resin of the outer layer; and

[C] spraying the material of the abrasion-resistant coating onto the thus-treated surface by means of a thermal spray process, thereby anchoring particles sprayed on the surface

to the particles by a chemical bond.

15. The method according to claim 14, wherein the particles have a size of from 10  $\mu\text{m}$  to 1,000  $\mu\text{m}$  and are incorporated in the outer layer in step [A] in an amount of 5 to 60% by volume relative to the total amount of the particles and the synthetic resin.

16. The method according to claim 15, wherein the particles and the abrasion-resistant coating layer are each made of a member selected from the group consisting of (a) nickel, chromium, vanadium, manganese, iron, cobalt, titanium, silicon or an alloy of one of these metals, (b) aluminium or an alloy thereof, (c) copper or an alloy thereof, (d) silicon dioxide, (e) aluminium dioxide, (f) titanium dioxide, (g) zirconium oxide and (h) silicon carbide/silicon.

17. The method according to claim 14, 15 or 16, wherein the plastic matrix of the body and the synthetic resin of the outer layer are of the same resin.

18. The method according to claim 17, wherein the resin is phenol formaldehyde resin.

FETHERSTONHAUGH & CO.  
OTTAWA, CANADA  
PATENT AGENTS